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Two luminescent complexes constructed from different metals with pyridine-2,4-dicarboxylic acid (H₂PDC)

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Two coordination complexes, [Mg(HPDC)₂(H₂O)₂] (**1**) and [Dy(PDC)₂(H₂O)₂]·5H₂O·NH₄ (**2**), were synthesized under hydrothermal conditions. The structures and fluorescent properties of the complexes were studied by elemental analysis, IR, thermal analysis, powder X-ray diffraction, and X-ray crystallography. In **1**, Mg(II) coordinated with six oxygens from H₂PDC and water. For **2**, there were NH₄⁺ ions in the holes of the metal quaternary rings to balance electronic charges. Compared to **1**, **2** constructed from Dy(III) had larger void space and potential applications on gas adsorption. The two complexes show similar fluorescence in the visible region.

Keywords: X-ray crystallography; Charge balance; Fluorescence properties

1. Introduction

Lanthanide(III) coordination complexes have attracted attention because of their potential applications in luminescence [1–5], magnetism [6–9], gas absorption [10], and sensors [11]. Narrow emission bands and relatively long luminescence lifetimes (as a result of transitions within the partially filled 4f shell of the ions [12]) make them candidates for a new type of luminescent material with applications such as fluoroimmunoassays and fluorescence microscopy [13]. Contrary to lanthanide coordination complexes, coordination polymers assembled by alkaline earth metal salts are seldom reported. This could result from unpredictable coordination numbers and geometries of alkaline earth metal ions since no ligand field stabilization effects govern their bonding [14]. However, they do offer the advantage of producing structurally interesting and diverse materials due to their interesting properties. The oxophilic nature of these metal ions renders them ideal candidates for coordination with oxygen donors [15]. Thermochemistry [14], biological, and catalytic activities [16] of such coordination polymers have been studied. However, little research regarding their fluorescence properties [17–19] has been done. Considering they are non-toxic, cheap, and generally amenable to aqueous preparation [20, 21], it is of great interest to develop new alkaline earth metal fluorescence materials.

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Pyridine-2,4-dicarboxylic acid (H₂PDC) is a multidentate ligand to fabricate functional materials, including porous materials adsorbing radicals [22], magnetic materials [23], and luminescent probes [17], which indicates that H₂PDC as a bridging ligand is an efficient way to construct useful materials. H₂PDC can form stable complexes with lanthanide and alkaline earth metals, giving self-assembled structures. We are interested in structures of complexes of metals from different groups with H₂PDC. Most lanthanide(III) coordination complexes are good luminescent materials, but alkaline earth metals are less studied. [Mg(HPDC)₂(H₂O)₂] (**1**) and [Dy(PDC)₂(H₂O)₂] \cdot 5H₂O \cdot NH₄ (**2**) were prepared by reacting H₂PDC with MgCl₂ \cdot 6H₂O or DyCl₃ \cdot 6H₂O. Single crystal X-ray diffraction revealed that every four Mg(II) or Dy(III) formed metal quarternary rings and HPDC⁻ or PDC²⁻ bridge, where carboxylate oxygens connect adjacent chelating rings to give an infinite 2-D network. In **2**, there was NH₄⁺ in the hole of every metal quarternary ring to balance the charge of the complex. The NH₄⁺ came from decomposition of H₂PDC under hydrothermal conditions; such decomposition has been rarely reported [24]. The complexes of Mg(II) and Dy(III) had similar luminescence in the visible region at excitation, implying the possibility for alkaline earth metal complexes as a new type of luminescent material.

2. Experimental

2.1. Materials and instruments

All reagents were purchased and used without purification unless specified. Elemental analyses (C, H, and N) were carried out on a Vario EL III CHNOS instrument made in Germany. Powder X-ray diffraction (PXRD) patterns were recorded on a Phillips PANalytical diffractometer for Cu K α radiation (λ = 1.5406 Å) with a scan speed of 2° min⁻¹ and a step size of 0.02° in 2 θ . The TG-DTG experiments for the complexes were performed using a NETZSCH STA 449C under nitrogen at 30 mL min⁻¹ with heating rate of 10 °C min⁻¹ from ambient temperature to 1000 °C. IR spectra were recorded on KBr disks on a BEQ, UZNDX-550 spectrometer.

2.2. Syntheses of the complexes

2.2.1. Syntheses of [Mg(HPDC)₂(H₂O)₂] (1**).** A mixture of MgCl₂ \cdot 6H₂O (20.3 mg, 0.1 mM), NaOH (8 mg, 0.2 mM), H₂PDC (16.7 mg, 0.1 mM), and CH₃OH (3 mL) was placed in a Parr Teflon-lined stainless steel vessel (25 mL). The vessel was sealed and heated at 433.15 K for four days. Then, the vessel was cooled to 373.15 K at 5 K h⁻¹ and slowly cooled to room temperature. The mixture was filtered and rectangular single crystals suitable for X-ray diffraction were obtained via evaporation. Yield: 12.8 mg, 65% (based on H₂PDC). Anal. Calcd for **1**: C, 42.86; H, 3.06; N, 7.14%. Found: C, 42.83; H, 3.05; N, 7.12%. IR bands (KBr pellets, cm⁻¹): 3421 sb, 1869 m, 1718 s, 1653 s, 1378 m, 1291s, 1242 m, 1159 w, 1080 w, 1012 m, 948 m, 795 w, 668 w.

2.2.2. Syntheses of [Dy(PDC)₂(H₂O)₂] \cdot 5H₂O \cdot NH₄ (2**).** A mixture of DyCl₃ \cdot 6H₂O (37.7 mg, 0.1 mM), NaOH (16.0 mg, 0.4 mM), H₂PDC (33.4 mg, 0.2 mM), and DMSO

(3 mL) was placed in a Parr Teflon-lined stainless steel vessel (25 mL), and the vessel was sealed and heated at 433.15 K for four days. Then, the vessel was cooled to 373.15 K at 5 K h⁻¹ and slowly cooled to room temperature. The mixture was filtered and rectangular single crystals suitable for X-ray diffraction were obtained directly by filtration. Yield: 32.7 mg, 77% (based on H₂PDC). Anal. Calcd for **2**: C, 26.39; H, 3.77; N, 6.60%. Found: C, 26.36; H, 3.76; N, 6.61%. IR bands (KBr pellets, cm⁻¹): 3428 sb, 2488 m, 1876 m, 1747 s, 1721 s, 1607 m, 1430 m, 1380 m, 1290 s, 1242 s, 1159 s, 1080 m, 993 s, 948 s, 883 w, 760 m, 668 m.

2.3. X-ray crystallography

Data were collected on a Bruker SMART CCD area-detector diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 293(2) K and data reduction was performed using Bruker SAINT [25]. The structures were solved with direct methods and refined by full matrix least-squares refinement on F^2 with anisotropic displacement parameters for non-H atoms using SHELXTL [26]. Hydrogens except for those of water were generated geometrically. Hydrogens of water were found in the difference Fourier map directly. The structural plots were generated with SHELXTL and Diamond [27, 28]. A summary of crystallographic data for the complexes is given in table 1. Selected bond lengths and angles are listed in table 2.

Table 1. Crystallographic data and structure refinement parameters for **1** and **2**.

Complex	1	2
Empirical formula	C ₁₄ H ₁₂ MgN ₂ O ₁₀	C ₁₄ H ₂₄ DyN ₃ O ₁₅
Formula weight	392.57	636.86
Temperature (K)	298(2)	298(2)
Crystal system	Monoclinic	Orthorhombic
Space group	<i>C2/c</i>	<i>Pbca</i>
<i>a</i> (Å)	10.0210(10)	14.8901(12)
<i>b</i> (Å)	9.4689(8)	9.8668(7)
<i>c</i> (Å)	16.4801(15)	28.694(3)
α (°)	90	90
β (°)	90.1320(10)	90
γ (°)	90	90
Volume (Å ³)	1563.8(2)	4215.6(6)
<i>Z</i>	4	8
D_{calc} (mg/m ³)	1.667	2.007
Absorption coefficient (mm ⁻¹)	0.178	3.629
<i>F</i> (000)	808	2520
Crystal size (mm)	0.18 × 0.08 × 0.06	0.20 × 0.16 × 0.13
Range <i>hkl</i> collected	-11 ≤ <i>h</i> ≤ 11 -11 ≤ <i>k</i> ≤ 10 -14 ≤ <i>l</i> ≤ 19	-17 ≤ <i>h</i> ≤ 17 -11 ≤ <i>k</i> ≤ 10 -34 ≤ <i>l</i> ≤ 30
Reflections collected/unique	4018/1385	20,259/3722
Completeness (%)	99.6	99.9
Data/restraints/parameters	1385/0/123	3722/0/298
Goodness-of-fit on F^2	1.066	1.058
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	$R_1 = 0.0664$ $wR_2 = 0.1104$	$R_1 = 0.0343$ $wR_2 = 0.0777$
Largest diff. peak and hole (eÅ ⁻³)	0.380 and -0.283	1.261 and -0.866

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1					
Mg1–O2A	2.317(3)	Mg1–O2B	2.317(3)	Mg1–O5	2.409(3)
Mg1–O5A	2.409(3)	Mg1–O1A	2.438(3)	Mg1–O1	2.438(3)
O2A–Mg1–O2B	106.09(17)	O2A–Mg1–O5	84.46(11)	O2B–Mg1–O5	83.46(12)
O2A–Mg1–O5C	83.46(12)	O2B–Mg1–O5C	84.46(11)	O5–Mg1–O5C	159.85(18)
O2A–Mg1–O1C	174.54(11)	O2B–Mg1–O1C	77.32(10)	O5–Mg1–O1C	100.27(10)
O5C–Mg1–O1C	92.72(11)	O2A–Mg1–O1	77.32(10)	O2B–Mg1–O1	174.54(11)
O5–Mg1–O1	92.72(11)	O5C–Mg1–O1	100.27(10)	O1C–Mg1–O1	99.62(16)
2					
Dy1–O7	2.310(3)	Dy1–O3	2.330(4)	Dy1–O1	2.338(3)
Dy1–O10	2.342(4)	Dy1–O9	2.345(4)	Dy1–O5	2.356(3)
Dy1–N2	2.585(4)	Dy1–N1	2.630(4)		
O7–Dy1–O3	93.82(13)	O7–Dy1–O1	139.36(12)	O3–Dy1–O1	80.33(13)
O7–Dy1–O10	148.90(11)	O3–Dy1–O10	95.35(14)	O1–Dy1–O10	71.60(12)
O7–Dy1–O9	90.77(14)	O3–Dy1–O9	146.67(12)	O1–Dy1–O9	74.89(13)
O10–Dy1–O9	97.56(15)	O7–Dy1–O5	79.08(13)	O3–Dy1–O5	140.02(12)
O1–Dy1–O5	129.39(13)	O10–Dy1–O5	74.85(13)	O9–Dy1–O5	73.22(13)
O7–Dy1–N2	78.41(13)	O3–Dy1–N2	75.51(12)	O1–Dy1–N2	136.52(13)
O1–Dy1–N2	75.27(14)	O9–Dy1–N2	137.59(13)	O5–Dy1–N2	64.52(13)
O7–Dy1–N1	74.96(12)	O3–Dy1–N1	73.53(13)	O1–Dy1–N1	64.77(13)
O10–Dy1–N1	136.13(13)	O9–Dy1–N1	75.88(14)	O5–Dy1–N1	138.94(13)
N2–Dy1–N1	137.20(14)				

3. Results and discussion

Through a number of experiments, we found that **1** tends to be dissolved by methanol, while **2** is more easily dissolved by DMSO. So $[\text{Mg}(\text{HPDC})_2(\text{H}_2\text{O})_2]$ (**1**) was synthesized in methanol and $[\text{Dy}(\text{PDC})_2(\text{H}_2\text{O})_2] \cdot 5\text{H}_2\text{O} \cdot \text{NH}_4$ (**2**) was synthesized in DMSO. Crystals of **1** were obtained via evaporation and crystals of **2** were obtained directly by filtration; both were characterized by X-ray crystallography.

3.1. Structural description

3.1.1. Structural analysis of $[\text{Mg}(\text{HPDC})_2(\text{H}_2\text{O})_2]$ (1**).** Single-crystal X-ray diffraction analysis of **1** revealed that the crystal system and space group of the complex are monoclinic, $C2/c$. The asymmetric unit of **1** consists of half a Mg(II), one HPDC[−], and one coordinated water. The coordination geometry around Mg(II) (figure 1) can be described as distorted octahedral with a coordination number of 6, where O1A, O2B, O5, and O5A form the equatorial plane, O1 and O2A are axial. Four of the six coordinated oxygens come from carboxylates and the others come from coordinated water. Nitrogens of pyridine rings do not coordinate. There are three Mg–O bond lengths, 2.317(3), 2.409(3), and 2.438(3) Å, with a mean value of 2.388(2) Å (table 2), which are longer than those reported for other Mg–O compounds ($[\text{Mg}(2,4\text{-PDC})(\text{H}_2\text{O})_3]$ and $[\text{Mg}(3,5\text{-PDC})(\text{H}_2\text{O})]$) [29]. The void space was calculated using PLATON, suggesting 15.9% void volume relative to the total crystal volume after removal of coordinated water (total potential solvent area volume: 248.6 Å³, per unit cell volume: 1563.8 Å³). The isomorphism of **1** has been reported by Mallick and co-workers [29]. In their work, $\text{Mg}(\text{CO}_2\text{CH}_3)_2 \cdot 4\text{H}_2\text{O}$ was used to react with H₂PDC under hydrothermal conditions, and a 0-D analog was obtained. In our case, the 2-D analog (figure 2) was synthesized when $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

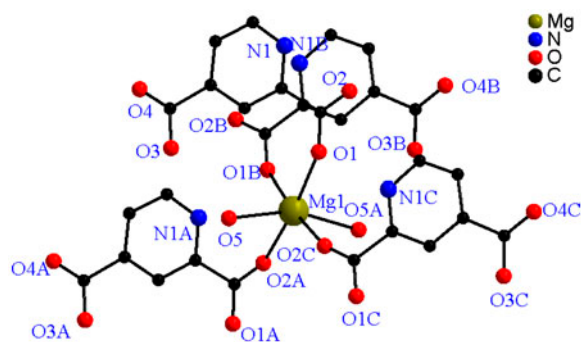


Figure 1. Coordination environment and polyhedron for Mg(II) in **1**. Probability ellipsoids are drawn at the 50% level. Lattice waters and hydrogens are omitted for clarity.

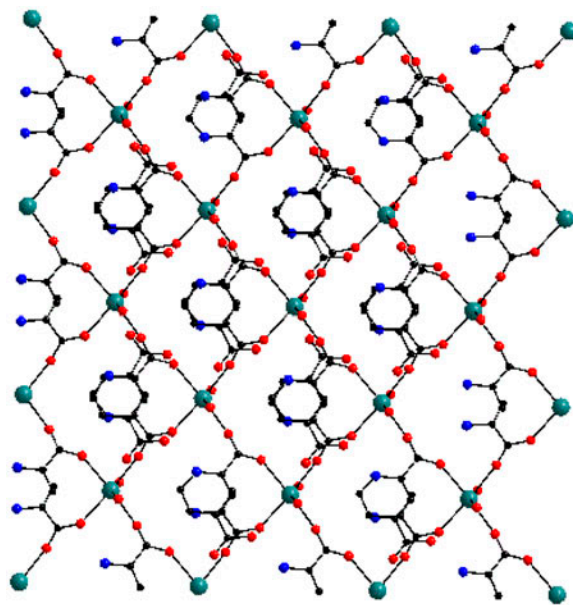


Figure 2. A fragment of the 2-D layer structure in **1**. Probability ellipsoids are drawn at the 50% level. Hydrogens are omitted for clarity.

reacted with H₂PDC, indicating that different metal salts could lead to different structures. Other structures have been reported involving alkaline earth metals with pyridine carboxylate. For example, Srinivasan and co-workers reported [Mg(H₂O)₅(3-npth)]·2H₂O coordination polymer based on 3-nitrophthalate. The use of 3-nitrophthalate resulted in six-coordinate Mg(II) which contained five coordinated waters. This compound could be considered as a molecular container for a water dimer [14]. In [Ba(in)(H₂O)₆][in] (inH=4-pyridinecarboxylic acid) reported by Rosado, the barium centers coordinated to carboxylate oxygens resulting in zigzag 1-D chains. These chains were associated into 2-D layers via hydrogen bonding and π - π interactions. The counter anion enabled linkage of the layers via an extensive network of hydrogen bonding and π - π interactions affording a

3-D framework [30]. These complexes constructed from alkaline earth metals and pyridine carboxylate exhibit low dimensional structure such as dimer, independent molecules, and 1-D chains. They are constructed to more complex structures by supramolecular interactions such as hydrogen bonding and π - π interactions. Compared to these compounds, **1** was a 2-D network assembled by coordination of Mg(II) and oxygens from H₂PDC. The 2-D network was constructed by covalent interactions, which are different from the structures reported. The pyridine rings were involved in π - π stacking interactions (centroid-to-centroid distance of 4.844 Å) with pyridine rings of neighboring faces along the *b* direction. Neighboring pyridine rings of the same face were involved in π - π stacking interactions (centroid-to-centroid distance of 3.689 Å) (figure 3). H-bonds in **1** are listed in table 3.

3.1.2. Structural analysis of [Dy(PDC)₂(H₂O)₂] \cdot 5H₂O \cdot NH₄ (2**).** Single-crystal X-ray diffraction analysis of **2** showed that the crystal system and space group are orthorhombic, *Pbca*. The asymmetric unit of **2** consists of one Dy(III), two PDC²⁻, one NH₄⁺, and seven waters (two are coordinated and five lattice waters). Like the lanthanide(III) coordination complexes [Eu(C₁₀H₆N₃O₅)₃(H₂O)₂] \cdot H₂O and [Tb(C₁₀H₆N₃O₅)₃(H₂O)₂] \cdot H₂O [31], the metal of **2** has a coordination number of 8. The coordination geometry around Dy(III) can be described as a distorted bicapped trigonal prism (figure 4), where O1, O3, and O10 formed the top plane of the trigonal prism and the bottom plane was completed by O9, O7, and O5, while N1 and N₂ capped two quadrilateral faces formed by O1, O3, O7, O9 and O31, O7, O5, O10, respectively. Unlike **1**, oxygen and nitrogen of PDC coordinated. The Dy-O_{carboxylate} bond lengths are 2.310(3)–2.356(3) Å (table 2) with a mean value of 2.337(3) Å, while Dy–N bond lengths are 2.585(4) and 2.630(4) Å (table 2) with a mean value of 2.608(4) Å. All bond lengths are similar to those reported for other Dy–O and Dy–N compounds [32]. Coordinated water (O9 and O10) and lattice water can be found in **2**. H-bonds in **2** are listed in table 3 and there were no π - π stacking interactions.

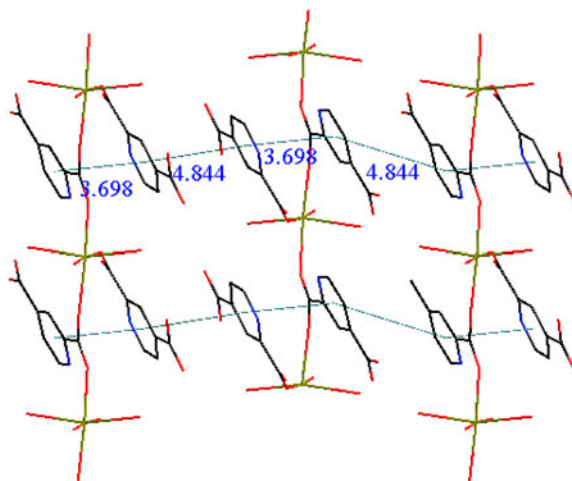
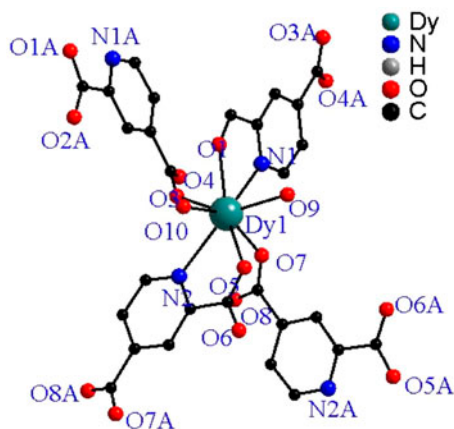


Figure 3. The π - π stacking interactions for **1**.

Table 3. Selected hydrogen bond lengths (Å) and angles (°) for **1** and **2**.

Donor–H···Acceptor	D–H	H···A	D···A	D–H···A
1				
N(1)–H(1)···O(2)	0.86	2.44	2.7558	102
N(1)–H(1)···O(1)	0.86	1.84	2.6896	171
O(5)–H(5C)···O(3)	0.85	2.24	3.0946	178
O(5)–H(5D)···O(4)	0.85	2.06	2.9081	177
C(4)–H(4)···O(3)	0.93	2.37	2.6992	101
C(7)–H(7)···O(5)	0.93	2.52	3.3603	151
C(7)–H(7)···O(2)	0.93	2.50	3.1819	131
2				
N(3)–H(3A)···O(6)	0.90	2.24	2.7566	116
N(3)–H(3A)···O(12)	0.90	2.55	3.4295	167
N(3)–H(3B)···O(13)	0.90	2.18	2.7305	119
N(3)–H(3C)···O(11)	0.90	1.95	2.8500	180
N(3)–H(3D)···O(9)	0.90	1.84	2.7377	179
O(9)–H(9C)···O(12)	0.85	1.82	2.6682	177
O(9)–H(9D)···O(11)	0.85	2.35	3.1978	178
O(10)–H(10C)···O(11)	0.85	1.89	2.7296	169
O(10)–H(10D)···O(15)	0.85	1.89	2.7267	170
O(11)–H(11C)···O(2)	0.85	1.96	2.8016	170
O(11)–H(11D)···O(5)	0.85	2.04	2.8835	170
O(12)–H(12C)···O(2)	0.85	1.92	2.7395	161
O(12)–H(12D)···O(6)	0.85	2.10	2.9165	162
O(13)–H(13C)···O(2)	0.85	2.15	2.9751	164
O(13)–H(13D)···O(14)	0.85	1.77	2.5983	163
O(14)–H(14C)···O(4)	0.85	1.66	2.4886	165
O(14)–H(14D)···O(8)	0.85	1.69	2.5180	165
O(15)–H(15C)···O(1)	0.85	2.12	2.9727	177
O(15)–H(15D)···O(6)	0.85	1.98	2.8324	177
C(4)–H(4)···O(13)	0.93	2.55	3.2885	136
C(7)–H(7)···O(7)	0.93	2.51	3.0931	121
C(13)–H(13)···O(4)	0.93	2.59	3.4892	162
C(14)–H(14)···O(3)	0.93	2.41	3.0229	124

Figure 4. Coordination environment and polyhedron for Dy(III) in **2**. Probability ellipsoids are drawn at the 50% level. Hydrogens are omitted for clarity.

Many structures involving other metals with pyridine carboxylate acid have been reported. For example, $[\text{Sm}_2\text{Cu}_3(\text{PDC})_6(\text{H}_2\text{O})_6]$ [33] and $[\text{Eu}(\text{C}_{10}\text{H}_6\text{N}_3\text{O}_5)_3(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ [31] possess a 3-D structure or a double chain structure, respectively. For **2**, as shown in figure 5, every four Dy(III) ions form metal quaternary rings and PDC^{2-} bridge with all carboxylate oxygens connecting the adjacent chelating rings to give an infinite 2-D network. In the hole of every metal quaternary ring, there was a NH_4^+ . Complex **2** was synthesized in DMSO under hydrothermal conditions, and H_2PDC decomposed and NH_3 released under high temperature and pressure. Then, NH_3 reacted with H^+ forming NH_4^+ . To prove decomposition of H_2PDC , H_2PDC by itself was placed under the same synthesis conditions in a Parr Teflon-lined stainless steel vessel (25 mL), and the vessel was sealed and heated at 433.15 K for four days. Then the vessel was cooled to room temperature and litmus test paper was placed upon the vessel when it was opened; the litmus test paper turned light blue, indicating NH_3 release from decomposing H_2PDC .

The distance between adjacent Dy(III) ions along the a axis is 14.8901(12) Å, while the distance along the b axis is 9.8668(8) Å. The void space was calculated using PLATON, suggesting a 4.8% void volume relative to the total crystal volume after the removal of NH_3 and lattice water (total potential solvent area volume: 200.6 Å³, per unit cell volume: 4215.6 Å³) (figure 6); however, this increased to 31.2% after removing coordinated water (total potential solvent area volume: 1316.6 Å³, per unit cell volume: 4215.6 Å³). The void volume of $[\text{Mg}(3,5\text{-PDC})(\text{H}_2\text{O})]$ (3,5- H_2PDC = 3,5-pyridine dicarboxylic acid) reported by Mallick and co-workers [29] was 11.9 and 38.7% after the removal of coordinated water. This compound was a good gas adsorber. This indicated that the complex would have the potential application on gas adsorption, which is rare compared to other complexes with only pyridine carboxylate and water coordinated to 4f-3d mixed metals [34, 35].

As shown in figure 7, the coordination of H_2PDC in **1** can be classified as μ_2 -(κ^2 , O^1 : O^2) with two 2-position carboxylate oxygens ($\text{O}1$ and $\text{O}2$) coordinated to $\text{Mg}1\text{A}(\text{II})$ and $\text{Mg}1(\text{II})$, respectively. The 4-position carboxylate oxygens ($\text{O}3$ and $\text{O}4$) and nitrogen did not coordinate. H_2PDC coordinated to two Mg(II) centers. Unlike **1**, H_2PDC in **2** adopted μ_2 -(κ^3 , O^1 : $\text{O}^{3\text{A}}$: N^1) coordination, connecting two Dy(III) ions. $\text{O}1$ of 2-position carboxyl-

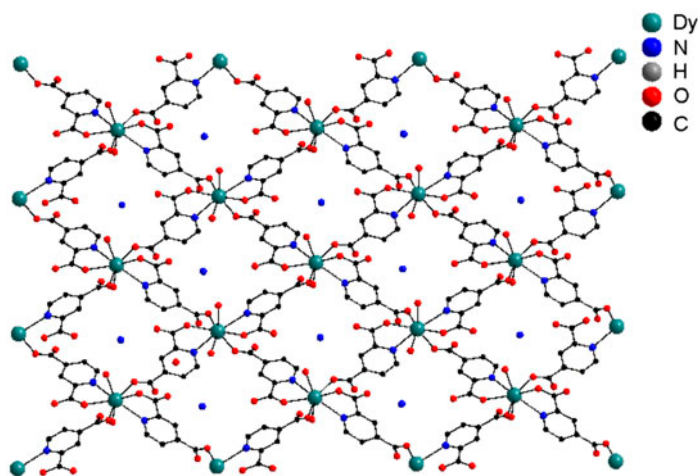


Figure 5. A fragment of the 2-D layer structure in **2**. Probability ellipsoids are drawn at the 50% level. Hydrogens are omitted for clarity.

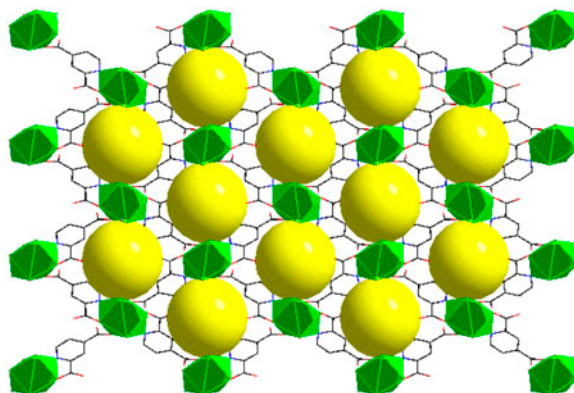


Figure 6. The void space after removal of NH_3 and lattice water in **2**. Probability ellipsoids are drawn at the 50% level. Hydrogens are omitted for clarity.

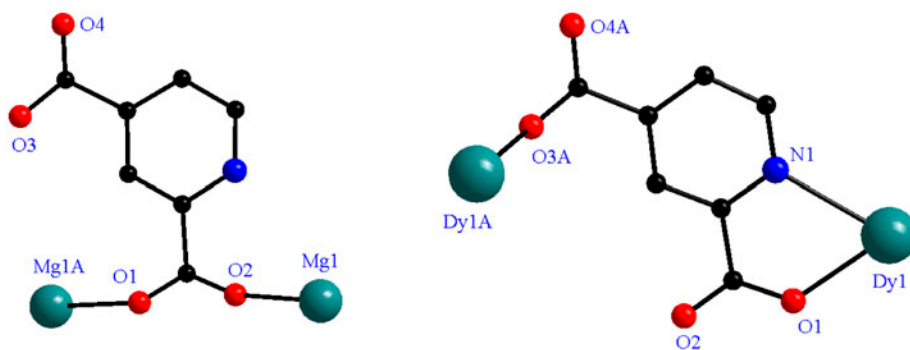


Figure 7. Coordination modes of H_2PDC in **1** and **2**. Probability ellipsoids are drawn at the 50% level.

ate and nitrogen of the ring chelate Dy1(III) and O3A of 4-position carboxylate coordinated to Dy1A(III) . Metal quaternary rings were formed in **1** and **2** via $\mu_2-(\kappa^2, \text{O}^1: \text{O}^2)$ or $\mu_2-(\kappa^3, \text{O}^1: \text{O}^{3A}: \text{N}^1)$, respectively. They share common edges in constructing a 2-D network with (4,4) topology, different from $[\text{EuCo}(\text{PDC})_3(\text{H}_2\text{O})_3]_n \cdot 2n\text{H}_2\text{O}$ and $[\text{YbCo}(\text{pydc})_3(\text{H}_2\text{O})_3]_n \cdot n\text{H}_2\text{O}$ possessing isostructural two-fold interpenetration corrugated brick wall layer structures with (6,3) topology [34].

3.2. Powder X-ray diffraction analysis and thermal analysis

The phase purities of **1** and **2** were characterized by PXRD. The experimental and computer-simulated PXRD patterns are shown in Supplementary Material. All major peaks of the experimental PXRD of the two complexes match quite well to those of the simulated PXRD, indicating reasonable crystalline phase purity. The thermal decompositions of **1** and **2** were characterized via TG-DTG. For **1**, two coordinated waters were lost (experimental weight loss was 9.92%; calculated weight loss was 9.28%) from 79 to 179 °C, then it collapsed, and finally transformed to MgCO_3 with experimental residue weight of

22.09% (calculated residue weight of 21.65%). The coordination complex **2** lost the absorbed NH_3 molecule and five lattice waters (experimental weight loss 16.95%; calculated weight loss 16.81%) at 72–202 °C, then the crystal lost two coordinated waters (experimental 5.98%; calculated 5.66%) from 202 to 227 °C; finally the crystal collapsed and transformed to Dy_2O_3 with experimental residue of 29.31% (calculated 29.30%). Water molecules and NH_3 in **2** were released without damaging the frameworks shown by the coincidence of the PXRD patterns of **2** heated and held at 120 °C in N_2 atmosphere with the PXRD patterns simulated from single-crystal structures. Also, pure **2** was placed in a vessel, and the vessel was sealed and heated at 120 °C; a red and wettish litmus test paper was placed on the vessel when it was opened, turning light blue, which indicated NH_3 release from decomposing **2**.

3.3. Fluorescence properties

The solid-state fluorescence spectra of **1** and **2** are shown in figure 8. To understand the nature of the emission band, fluorescence of H_2PDC in solid state was also investigated at room temperature. Free H_2PDC had very weak fluorescence upon photoexcitation at 305 nm (almost could not be detected), while **1** and **2** exhibited intense photoluminescence with maximum emission at 480 and 575 nm upon excitation at 305 nm.

Previous studies [36, 37] found that a heterocyclic aromatic ligand can effectively decrease π and π^* orbital energies. Thus, the HOMO and LUMO of complexes may lack contribution from metal. The energy absorbed by the ligand cannot transfer to metal, and the LMCT emission can be excluded. Photoluminescence mechanism of coordination complexes mainly depends on the nature of the ligand [32, 34]. The similarity of the emission spectra of **1** and **2** indicates that a ligand-centered $\pi \rightarrow \pi^*$ excitation is responsible for the emissions. The luminescence intensity increase when coordinated to $\text{Mg}(\text{II})$ and $\text{Dy}(\text{III})$ may be attributed to increased rigidity of H_2PDC on coordination, reducing nonradiative relaxation.

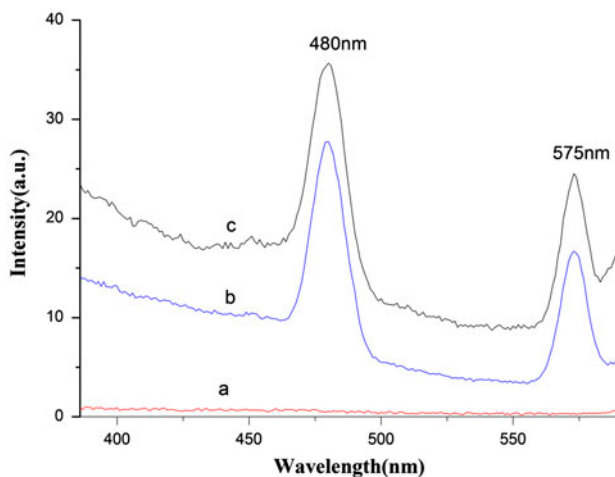


Figure 8. Solid-state emission spectrum of H_2PDC (a), **1** (b), and **2** (c) at room temperature.

4. Conclusions

Mg(II) and Dy(III) coordination polymers constructed from H₂PDC were synthesized. X-ray crystallography disclosed that both complexes were constructed by 2-D network with (4,4) topology. In **1**, Mg(II) coordinates to oxygen from H₂PDC. Compared to **1**, **2** has a larger void space and shows potential application for gas adsorption. The polymer of Mg(II) showed similar fluorescence to that of the polymer of Dy(III) in the visible region upon excitation, implying complexes constructed by alkaline earth metals also have good fluorescence properties. Thus, a new type of alkaline earth metal fluorescence material can be achieved in this way.

Supplemental material

Supplementary data are available from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (Fax:+44-1233-336033; E-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>) on request quoting Deposit Nos. 900784 and 900785.

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References

- [1] M. Chen, M.-S. Chen, T.-A. Okamura, M.-F. Lv, W.-Y. Sun, N. Ueyama. *Cryst. Eng. Comm.*, **13**, 3801 (2011).
- [2] K.T. Hua, J. Xu, E.E. Quiroz, S. Lopez, A.J. Ingram, V.A. Johnson, A.R. Tisch, A. de Bettencourt-Dias, D. A. Straus, G. Muller. *Inorg. Chem.*, **51**, 647 (2011).
- [3] J. Rocha, L.D. Carlos, F.A.A. Paz, D. Ananias. *Chem. Soc. Rev.*, **40**, 926 (2011).
- [4] L.D. Wang, F. Tao, M.L. Cheng, Q. Liu, W. Han, Y.J. Wu, D.D. Yang, L.J. Wang. *J. Coord. Chem.*, **65**, 923 (2012).
- [5] X.Q. Cao, X. Zheng, M.X. Chen, X.X. Xu, T. Sun, E.B. Wang. *J. Coord. Chem.*, **65**, 754 (2012).
- [6] P.E. Car, M. Perfetti, M. Mannini, A. Favre, A. Caneschi, R. Sessoli. *Chem. Commun.*, **47**, 3751 (2011).
- [7] S.M. Fang, E.C. Sañudo, M. Hu, Q. Zhang, S.T. Ma, L.R. Jia, C. Wang, J.Y. Tang, M. Du, C.S. Liu. *Cryst. Growth Des.*, **11**, 811 (2011).
- [8] J. Long, F. Habib, P.-H. Lin, I. Korobkov, G. Enright, L. Ungur, W. Wernsdorfer, L.F. Chibotaru, M. Murugesu. *J. Am. Chem. Soc.*, **133**, 5319 (2011).
- [9] M.F. Wu, M.S. Wang, S.P. Guo, F.K. Zheng, H.F. Chen, X.M. Jiang, G.N. Liu, G.C. Guo, J.S. Huang. *Cryst. Growth Des.*, **11**, 372 (2011).
- [10] B. Cai, P. Yang, J.W. Dai, J.Z. Wu. *Cryst. Eng. Comm.*, **13**, 985 (2011).
- [11] I. Leonenko, D. Aleksandrova, A. Yegorova, V. Antonovitch, S. Basok. *J. Anal. Chem.*, **66**, 158 (2011).
- [12] Z.-H. Zhang, Y. Song, T.-A. Okamura, Y. Hasegawa, W.-Y. Sun, N. Ueyama. *Inorg. Chem.*, **45**, 2896 (2006).
- [13] D. Parker, R.S. Dickins, H. Puschmann, C. Crossland, J.A.K. Howard. *Chem. Rev.*, **102**, 1977 (2002).
- [14] B.R. Srinivasan, S.Y. Shetgaonkar, C. Näther. *Z. Anorg. Allg. Chem.*, **637**, 130 (2011).
- [15] N.R. Kelly, S. Goetz, S.R. Batten, P.E. Kruger. *Cryst. Eng. Comm.*, **10**, 68 (2008).
- [16] T.M.A. Al-Shboul, G. Volland, H. Görls, M. Westerhausen. *Z. Anorg. Allg. Chem.*, **635**, 1568 (2009).
- [17] X.Q. Zhao, Y. Zuo, D.L. Gao, B. Zhao, W. Shi, P. Cheng. *Cryst. Growth Des.*, **9**, 3948 (2009).
- [18] B. Valeur, I. Leray. *Coord. Chem. Rev.*, **205**, 3 (2000).

- [19] S. Fery-Forgues, M.T. Le Bris, J.P. Guette, B. Valeur. *J. Phys. Chem.*, **92**, 6233 (1988).
- [20] P. Dröse, S. Blaurock, C.G. Hrib, F.T. Edelmann. *Z. Anorg. Allg. Chem.*, **637**, 186 (2010).
- [21] W.Z. Zhang, T.Y. Lv, D.Z. Wei, R. Xu, G. Xiong, Y.Q. Wang, E.J. Gao, Y.G. Sun. *Inorg. Chem. Commun.*, **14**, 1245 (2011).
- [22] X.Q. Zhao, B. Zhao, Y. Ma, W. Shi, P. Cheng, Z.H. Jiang, D.Z. Liao, S.P. Yan. *Inorg. Chem.*, **46**, 5832 (2007).
- [23] H.-L. Gao, L. Yi, B. Zhao, X.-Q. Zhao, P. Cheng, D.-Z. Liao, S.-P. Yan. *Inorg. Chem.*, **45**, 5980 (2006).
- [24] S. Siegfried, S. Helmut, R. Alfred, T. Johannes. *Freiberg. Forschungsh. A*, **795**, 79 (1989).
- [25] Siemens: Area Detector Control and Intergration Software. *Version 5.0, SMART and SAINT, Siemens Analytical X-ray Instruments*, Madison, WI (1998).
- [26] G.M. Sheldrick. *SHELXS 97, Program for Crystal Structure Solution*, University of Gottingen, Gottingen (1997).
- [27] O.V. Dolomanov, A.J. Blake, N.R. Champness, M. Schroder. *J. Appl. Crystallogr.*, **36**, 1283 (2003).
- [28] A.L. Spek. *Implemented as the PLATON procedure, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht (1998).
- [29] A. Mallick, S. Saha, P. Pachfule, S. Roy, R. Banerjee. *J. Mater. Chem.*, **20**, 9073 (2010).
- [30] P.J. Rosado, K.R. Senge. *J. Coord. Chem.*, **64**, 186 (2011).
- [31] L.-Z. Chen, F.-M. Wang, H. Shu. *J. Coord. Chem.*, **65**, 439 (2012).
- [32] Y.G. Sun, G. Xiong, M.Y. Guo, F. Ding, L. Wang, E.J. Gao, M.C. Zhu, F. Verpoort. *Z. Anorg. Allg. Chem.*, **637**, 293 (2010).
- [33] Y. Liang, R. Cao, M.C. Hong, D.F. Sun, Y.J. Zhao, J.B. Weng, R.H. Wang. *Inorg. Chem. Commun.*, **5**, 366 (2002).
- [34] Y.G. Huang, M.Y. Wu, F.Y. Lian, F.L. Jiang, M.C. Hong. *Inorg. Chem. Commun.*, **11**, 840 (2008).
- [35] S. Sharif, O. Sahin, I.U. Khan, O. Büyükgüngör. *J. Coord. Chem.*, **65**, 1892 (2012).
- [36] S.L. Zheng, J.H. Yang, X.L. Yu, X.M. Chen, W.T. Wong. *Inorg. Chem.*, **43**, 830 (2003).
- [37] J.F. Song, R.S. Zhou, T.P. Hu, Z. Chen, B.B. Wang. *J. Coord. Chem.*, **63**, 4201 (2010).